

# MORE ON THE POSSIBLE COMPOSITION OF THE MERIDIANI HEMATITE-RICH CONCRETIONS.

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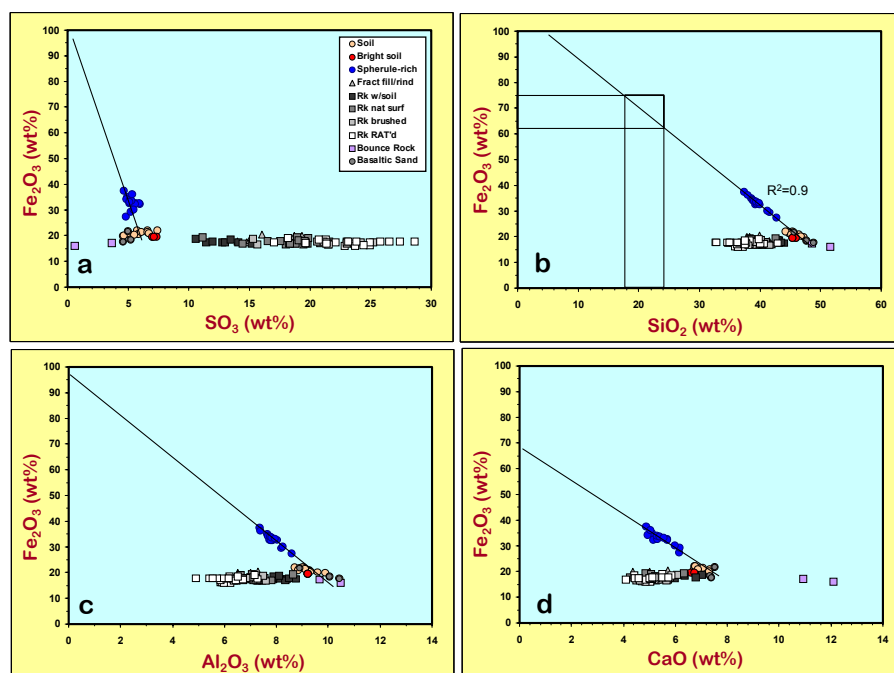
**Introduction:** Elsewhere in these proceedings, Schneider et al. [1] discuss compositional constraints on hematite-rich spherule (blueberry) formation at Meridiani Planum. Schneider et al. provide the background for work done to date to understand the composition and mineralogy of the spherules and devise a test of possible concretion growth processes. They also report the results of area analyses of spherules in targets analyzed with the Alpha Particle X-ray Spectrometer (APXS) and test several possible models for included components other than hematite.

In this abstract, we use the compositional trends for spherule-rich targets to compute possible elemental compositions of the spherules. This approach differs from that of [2], which also used a determination of the area of spherules in APXS targets, coupled with a correction for the radial acceptance function, to try to unmix the compositions directly, using 2 and 3-component models and mass balance. That approach contained a fair amount of uncertainty owing to problems associated with irregular and heterogeneous target geometry, unknown composition of non-spherule lithic components, and variable dust coatings on spherules. Since then, Opportunity has analyzed additional spherule-rich targets, and the compositional trends so obtained permit a more direct assessment of the data, as is also the case in the work of [1].

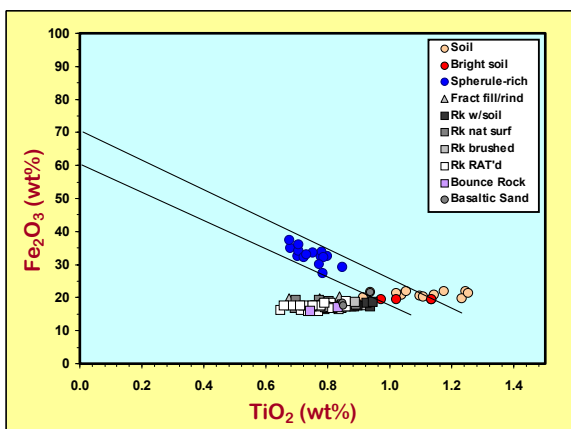
**APXS Data:** Opportunity has now measured with the APXS the compositions of over 10 spherule-rich targets [3,4]. Most of these targets consist of some combination of spherules and soil, although the “Berrybowl” target in Eagle crater consisted of spherules on a thin patch of soil in a depression in a flat exposure of sulfate-rich outcrop. Compositions obtained from the spherule-rich targets are Fe-rich, ranging from ~28 to 38 wt.%  $\text{Fe}_2\text{O}_3(\text{T})$ .

For some elements, correlations with  $\text{Fe}_2\text{O}_3$  are strong and fairly linear, thus these can be treated to first approximation as a linear, 2-component mixing system (spherules and soil), and we can calculate the  $\text{Fe}_2\text{O}_3$ -rich composition to which the data extrapolate. For some elements such as  $\text{Al}_2\text{O}_3$  and  $\text{SO}_3$  (Fig. 1), the correlation projects within uncertainty to 100%  $\text{Fe}_2\text{O}_3$ ; if all elements did likewise, then pure hematite spherules would be indicated, but they do not. For two of the elements shown in Fig. 1,  $\text{SiO}_2$  and  $\text{CaO}$ , the extrapolations do not project to 100%  $\text{Fe}_2\text{O}_3$ . For  $\text{SiO}_2$ , the extrapolation requires that there be some  $\text{SiO}_2$  in the spherules. For  $\text{CaO}$ , which projects to ~70%  $\text{Fe}_2\text{O}_3$  at 0%  $\text{CaO}$ , an upper limit of ~70%  $\text{Fe}_2\text{O}_3$  in the spherules is indicated (Fig. 1d).

Other elements behave similarly to Ca, including Ti, Cr, and K, and several elements, such as Cl and P, show little variation from the soils as a function of  $\text{Fe}_2\text{O}_3$ . For some elements, the correlation with Fe exhibits more scatter than, for example, Si and Al. In cases such as these (see for example,  $\text{TiO}_2$ , Fig. 2), it is not clear which is the most appropriate soil composition to use as the soil end-member. Uncertainty in the data also contribute to scatter, especially for some of the minor elements. For the purpose of extrapolat-



**Figure 1.** Correlations between Fe (total as  $\text{Fe}_2\text{O}_3$ ) and other elements. Some extrapolate to hematite (100%  $\text{Fe}_2\text{O}_3$ ) whereas others do not. Lines in b illustrate graphically the solution space for spherule compositions described in the text.

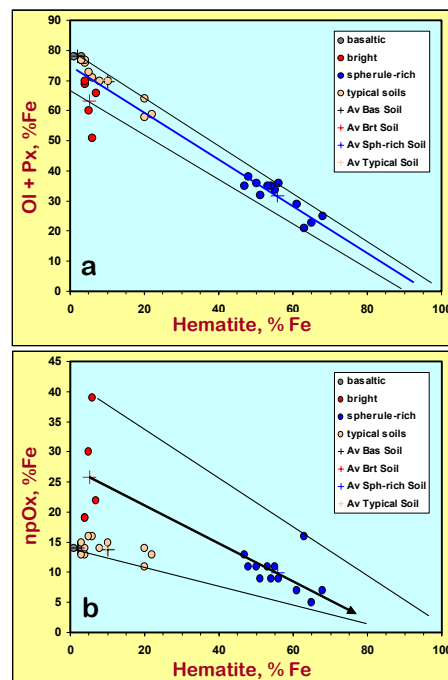


**Figure 2.** Extrapolation from soil compositions through spherule compositions indicates the spherules have <100% hematite.

ing trends to the Fe-rich spherule composition, the average composition of the spherule-rich targets is used with two different average spherule-poor soil compositions, (1) an average of 16 soils, and (2) an average of three “bright” or sulfate-rich soils. A range of solutions is possible; here we show results of these two models as representative examples.

In these models, we vary the soil:spherule proportions and calculate the spherule compositions using simple mass balance. As the ratio of soil to spherules increases, calculated  $\text{Fe}_2\text{O}_3$  in the spherules increases up to the point at which concentrations of one or more of the other elements goes to zero, and this sets an upper limit to  $\text{Fe}_2\text{O}_3$ . For model 1, this occurs at  $\text{Fe}_2\text{O}_3 \sim 62$  wt% and a soil:spherule ratio of 68:32. Ti and Cr go to zero first, followed by Ca at a soil:spherule ratio of 75:25. Model spherule compositions (Table 1) are not unique; what is important are the upper limits imposed on  $\text{Fe}_2\text{O}_3$ .

**Mössbauer Data:** Opportunity has also measured over 10 spherule-rich targets with the Mössbauer spectrometer [5,6]. Considering also the spherule-poor soils and from a graphical analysis similar to that used for the APXS data, the trends for pyroxene + olivine vs. hematite extrapolate very nearly to 100% hematite (Fig. 3a). In this plot, it is not obvious which soil component should be used to constrain the trends. The correlation of np-Ox vs. hematite (Fig. 3b) suggests that an average composition for the bright soils (i.e., the most dusty ones) is the appropriate soil composition for the MB trends. Using this for pyroxene plus olivine suggests that some (pyroxene) should be present, but accounting for <10% of the Fe. Thus there is reason to conclude that the spherules contain on or



**Figure 3.** Percentage of Fe in different phases in Meridiani soils and spherule-rich targets. Crosses represent averages of bright soils, spherule-poor soils, and spherule-rich soils. Mössbauer spectrometer results from [6].

der of 5-10% pyroxene, and all the rest of the Fe is hematite. In the sulfate-rich outcrop, 90% of the Fe is oxidized and present either as  $\text{Fe}^{3+}$  oxide or  $\text{Fe}^{3+}$  sulfate [6]. The models presented here are consistent with concretions having replaced the sulfate (jarosite+ $\text{Fe}_3\text{D}_3$ ) with hematite, but having included the pyroxene. This analysis refers to Fe-pyroxene; however, there is some amount of Mg present according to the compositional models. Some of the Mg can be tied up in pyroxene, increasing its total weight proportion. The model presented here requires laboratory verification by analysis of mixed targets of similar geometry and dust coatings to the Meridiani spherules.

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**References:** [1] Schneider et al. (2007) *LPS* 38, These Proceedings; [2] Jolliff et al. (2005) *LPS* 36, #2269. [3] Rieder, R. et al., 2004, *Science* 306, 1746-1749. [4] Gellert et al., 2007, *JGR*, in press; [5] Klingelhöfer, G. et al., 2004, *Science* 306, 1740-1745; [6] Morris et al., 2006, *JGR*, 111, E12S15.

**Model Spherule compositions**

odel oil fraction	1	2	1	2
SiO <sub>2</sub>	24.7	25.5	18.3	19.5
TiO <sub>2</sub>	0.04	0.10	-0.27	-0.19
Al <sub>2</sub> O <sub>3</sub>	4.44	4.59	2.99	3.20
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.13	-0.13	0.06
FeO	55.3	57.3	66.4	69.2
MnO	0.09	0.14	0.00	0.08
MgO	5.22	4.78	4.58	3.94
NiO	0.24	0.21	0.29	0.26
CaO	1.61	2.27	0.00	0.95
Na <sub>2</sub> O	2.19	2.17	2.19	2.15
K <sub>2</sub> O	0.17	0.13	0.08	0.02
P <sub>2</sub> O <sub>5</sub>	0.78	0.73	0.77	0.69
SO <sub>3</sub>	4.32	1.42	3.90	-0.30
Cl	0.90	0.57	0.99	0.51

Model 1 uses Av spherule-poor soil, n=16.

Model 2 uses Av bright (SO<sub>3</sub>-rich) soil, n=3.

All Fe listed as FeO.

**Table 1.** Modeled spherule compositions with values shown in red going to zero or negative.